

CLAIMS

We claim:

1. A removable, water-whitening resistant pressure sensitive adhesive comprising a crosslinked aqueous emulsion polymer comprising:

- 5 (a) at least one hydrophobic monomer selected from an alkyl (meth)acrylate ester of an alcohol wherein the alkyl portion of the alcohol is linear or branched and contains at least 4 carbon atoms, or a mixture of at least one styrenic monomer and at least one alkyl (meth)acrylate ester of an alcohol wherein the alkyl portion of the
- 10 alcohol is linear or branched and contains at least 4 carbon atoms, wherein when a styrenic monomer is present, said styrenic monomer is present in an amount up to about 30 wt. % of the total hydrophobic monomer mixture;
- (b) at least about 2 wt. % of at least one hydrophilic monomer; and
- 15 (c) at least about 5 wt. % of at least one partially hydrophilic monomer selected from alkyl (meth)acrylate esters of an alcohol wherein the alkyl portion of the alcohol has 1 to 2 carbon atoms, N-vinyl-2-pyrrolidone, or mixtures thereof;

wherein said crosslinked aqueous emulsion polymer is crosslinked with at

20 least one polyfunctional aziridine crosslinker, and the wt. % of monomers (a), (b), and (c) are based on the total weight of monomers (a), (b), and (c).

2. The composition of claim 1 wherein the amount of monomer (a) in said crosslinked aqueous emulsion polymer is about 50 to about 90 wt. %.

25 3. The composition of claim 2 wherein the amount of monomer (a) in said crosslinked aqueous emulsion polymer is about 70 to about 90 wt. %.

4. The composition of claim 1 wherein the amount of monomer (b) in said crosslinked aqueous emulsion polymer is about 2 to about 10 wt. %.

5. The composition of claim 4 wherein the amount of monomer (b) in

said crosslinked aqueous emulsion polymer is about 3 to about 8 wt. %.

6. The composition of claim 1 wherein the amount of monomer (c) in said crosslinked aqueous emulsion polymer is about 5 to about 25 wt. %.

7. The composition of claim 6 wherein the amount of monomer (c) in said crosslinked aqueous emulsion polymer is about 8 to about 20 wt. %.

8. The composition of claim 1 wherein the pH of said aqueous emulsion polymer is at least 6.

9. The composition of claim 8 wherein the pH of said aqueous emulsion polymer is about 6.5 to about 9.

10. The composition of claim 1 wherein said removable, water-whitening resistant pressure sensitive adhesive has a peel strength of less than about 2.5 pounds per inch peel force with adhesive failure mode.

11. The composition of claim 1 wherein said monomer (a) is selected from isooctyl acrylate, 4-methyl-2-pentyl acrylate, 2-methylbutyl acrylate, isoamyl acrylate, sec-butyl acrylate, n-butyl acrylate, 2-ethylhexyl acrylate, isodecyl methacrylate, isononyl acrylate, isodecyl acrylate, or mixtures thereof.

12. The composition of claim 11 wherein said monomer (a) is selected from n-butyl acrylate, 2-ethylhexyl acrylate, or mixtures thereof.

13. The composition of claim 1 wherein said monomer (b) is selected from a monoolefinic monocarboxylic acid, a monoolefinic dicarboxylic acid, 2-hydroxyethyl acrylate, or mixtures thereof.

14. The composition of claim 13 wherein said monomer (b) is selected from acrylic acid, methacrylic acid, fumaric acid, maleic acid, itaconic acid, crotonic acid, 2-hydroxyethyl acrylate, or mixtures thereof.

15. The composition of claim 14 wherein said monomer (b) is selected from acrylic acid, 2-hydroxyethyl acrylate, or mixtures thereof.

16. The composition of claim 1 wherein said monomer (c) is selected from methyl acrylate, methyl methacrylate, ethyl acrylate, or mixtures thereof.

17. The composition of claim 16 wherein said monomer (c) is selected from methyl acrylate, methyl methacrylate, or mixtures thereof.

5 18. The composition of claim 1 wherein said aqueous emulsion polymer further comprises a surfactant selected from a non-polymerizable surfactant, a polymerizable surfactant, or mixtures thereof.

19. The composition of claim 18 wherein said surfactant comprises a non-polymerizable surfactant.

10 20. The composition of claim 19 wherein said non-polymerizable surfactant is selected from an ionic surfactant or a mixture of an ionic surfactant and a nonionic surfactant.

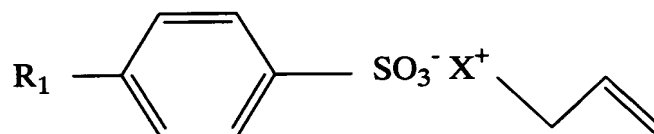
21. The composition of claim 20 wherein said ionic surfactant is an anionic surfactant selected from alkyl aryl sulfonates, alkyl sulfates, sulfates of
15 ethoxylated alcohols, sulfates and sulfonates of ethoxylated alkylphenols, sulfosuccinates, diphenyl sulfonates, or mixtures thereof.

22. The composition of claim 18 wherein said surfactant is at least one water-soluble or water-dispersible polymerizable surfactant selected from compounds having a terminal allyl amine moiety, substituted phenyl compounds having at least
20 one alkenyl substituent, polyoxyalkylene-1-(allyloxymethyl) alkyl ether sulfate salts, or mixtures thereof.

23. The composition of claim 22 wherein said polymerizable surfactant has a hydrophilic portion selected from a sulfonate allyl amine moiety, a sulfate allyl amine moiety, or a phosphate allyl amine moiety, and a hydrophobic portion selected
25 from -R, or a group having the formula $\text{RO}-(\text{CH}_2\text{CH}_2\text{O})_n-$; wherein R is an alkyl group or an alkyl-substituted phenyl group wherein the alkyl group has 1 to 20 carbon atoms, and n is an integer from 2 to 100.

24. The composition of claim 23 wherein n is an integer from 2 to 15.

25. The composition of claim 22 wherein said polymerizable surfactant is an allyl amine salt of an alkyl benzene sulfonate having the formula



5 wherein R₁ is an alkyl group having 1 to 20 carbon atoms, and X⁺ is selected from ⁺NH₃, ⁺NH₂R₄, or ⁺NHR₄R₅, wherein R₄ and R₅ are independently selected from C₁-C₄ alkyl or hydroxyalkyl groups.

26. The composition of claim 25 wherein said polymerizable surfactant is an allyl amine salt of dodecylbenzene sulfonate.

27. The composition of claim 22 wherein said polymerizable surfactant is an allyl amine salt of an alkyl ether sulfate having the formula

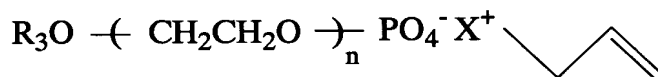


5 wherein R_2 is an alkyl group having 1 to 20 carbon atoms, n is an integer from 2 to 100, and X^+ is selected from $^+NH_3$, $^+NH_2R_4$, or $^+NHR_4R_5$, wherein R_4 and R_5 are independently selected from C_1 - C_4 alkyl or hydroxyalkyl groups.

28. The composition of claim 27 wherein n is an integer from 2 to 15.

29. The composition of claim 28 wherein said polymerizable surfactant is
10 an allyl amine salt of laureth sulfate.

30. The composition of claim 22 wherein said polymerizable surfactant is an allyl amine salt of a phosphate ester having the formula



15 wherein R_3 is an alkyl or alkyl-substituted phenyl group wherein the alkyl group has 1 to 20 carbon atoms, n is an integer from 2 to 100, and X^+ is selected from $^+NH_3$, $^+NH_2R_4$, or $^+NHR_4R_5$, wherein R_4 and R_5 are independently selected from C_1 - C_4 alkyl or hydroxyalkyl groups.

31. The composition of claim 30 wherein n is an integer from 2 to 15.

32. The composition of claim 31 wherein said polymerizable surfactant is
20 an allyl amine salt of nonylphenol ethoxylate (9 moles EO) phosphate ester.

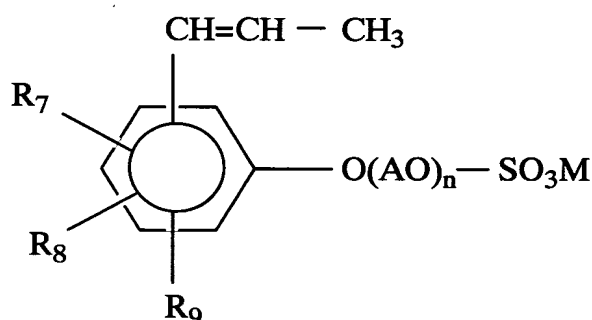
33. The composition of claim 22 wherein said polymerizable surfactant is an allyl amine salt of a sulfate having the formula



wherein R_6 is an alkyl group having 6 to 20 carbon atoms, and X^+ is selected from $^+NH_3$, $^+NH_2R_4$, or $^+NHR_4R_5$, wherein R_4 and R_5 are independently selected from C_1 - C_4 alkyl or hydroxyalkyl groups.

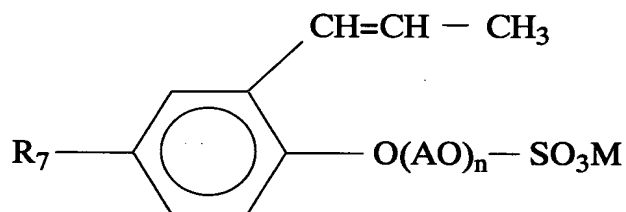
34. The composition of claim 31 wherein R_6 is an alkyl group having 10 to 18 carbon atoms.

35. The composition of claim 22 wherein said polymerizable surfactant is a substituted phenyl compound having the formula



wherein R_7 is an alkyl, alkenyl or aralkyl group containing 6 to 18 carbon atoms; R_8 is a hydrogen atom or an alkyl, alkenyl or aralkyl group containing 6 to 18 carbon atoms; R_9 is a hydrogen atom or a propenyl group; A is an unsubstituted or substituted alkylene group containing 2 to 4 carbon atoms; n is an integer of 1 to about 200; and M is an alkali metal, an ammonium ion, or an alkanolamine residue.

36. The composition of claim 35 wherein said polymerizable surfactant is a substituted phenyl compound having the formula

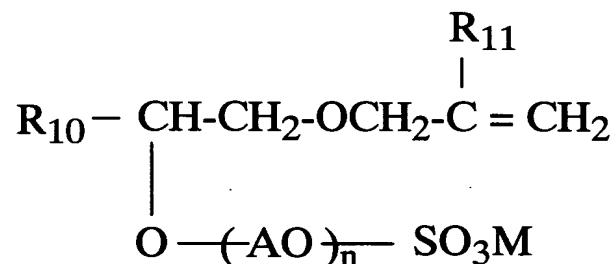


37. The composition of claim 36 wherein R_7 is alkyl, A is ethylene, and M

is alkali metal or ammonium.

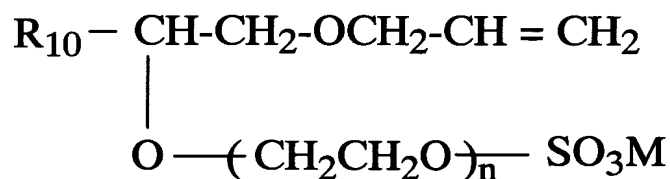
38. The composition of claim 37 wherein R₇ is nonyl, n is about 10 to about 30, and M is ammonium.

39. The composition of claim 22 wherein said polymerizable surfactant is
5 a polyoxyalkylene-1-(allyloxymethyl) alkyl ether sulfate salt having the formula:



wherein R₁₀ is an alkyl group containing 8 to 30 carbon atoms; R₁₁ is
hydrogen or methyl; A is an unsubstituted or substituted alkylene
group having 2 to 4 carbon atoms; n is 0 or an integer of 1 to about
10 200; and M is an alkali metal, an ammonium ion, or an alkanolamine
residue.

40. The composition of claim 39 wherein said polymerizable surfactant is
a polyoxyalkylene-1-(allyloxymethyl) alkyl ether sulfate salt having the formula:



15 wherein R₁₀ is an alkyl group containing 8 to 14 carbon atoms; and n is an
integer of 1 to about 200.

41. The composition of claim 18 wherein said surfactant is a mixture of an
ionic non-polymerizable surfactant and a water-soluble or water-dispersible
20 polymerizable surfactant selected from compounds having a terminal allyl amine

moiety, substituted phenyl compounds having at least one alkenyl substituent, polyoxyalkylene-1-(allyloxymethyl) alkyl ether sulfate salts, or mixtures thereof.

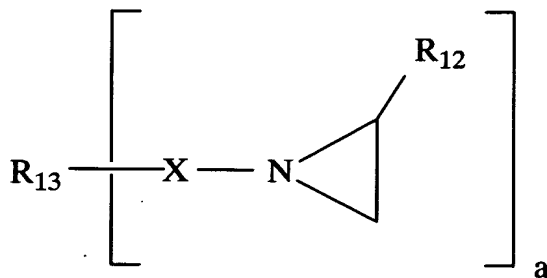
42. The composition of claim 1 wherein said polyfunctional aziridine is a compound having at least two nitrogen atoms wherein at least one of the nitrogen atoms is in an aziridine ring and at least one of the nitrogen atoms is contained in a side chain bonded to the aziridine nitrogen.

43. The composition of claim 42 wherein said polyfunctional aziridine is selected from N-aminoethyl-N-aziridylethylamine, N,N-bis-2-aminopropyl-N-aziridylethylamine, or N-3,6,9-triazanonyl-aziridine.

44. The composition of claim 1 wherein said polyfunctional aziridine is a compound having at least two aziridine groups.

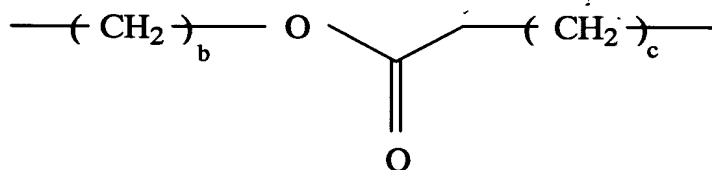
45. The composition of claim 44 wherein said polyfunctional aziridine is selected from bisaziridines of diacrylates of alkoxyated polyols, trisaziridines of triacrylates of alkoxyated polyols, or mixtures thereof.

46. The composition of claim 44 wherein said polyfunctional aziridine is selected from polyaziridines represented by the formula



wherein R₁₂ is hydrogen or an alkyl group having 1 to 10 carbon atoms, optionally substituted by groups which do not interfere with the crosslinking reaction; R₁₃ is a direct bond or an aliphatic radical having 1 to 30 carbon atoms, optionally substituted by hydroxy, halogen, or C₁ to C₁₂ alkoxy; X is an alkylene group having 1 to 30 carbon atoms, optionally containing an ester group, an ether group, or an amide group; and a is 2 to 4.

47. The composition of claim 46 wherein R_{12} is selected from hydrogen, methyl, ethyl, propyl or butyl, X is represented by the formula



wherein b is 1 to 3 and c is 1 to 3; a is 2 to 3; and R_{13} is a propylene radical or a 2-hydroxyethyl radical.

48. The composition of claim 46 wherein said polyaziridine is selected from trimethylolpropane tris[([β]-N-aziridiny)propionate], pentaerythritol tris[([β]-N-aziridiny)propionate], trimethylolpropane tris[([β]-N-2-methyl-1-aziridiny)propionate], or mixtures thereof.

49. The composition of claim 1 wherein the amount of aziridine groups in said polyfunctional aziridine crosslinker is at least 0.01 equivalents per equivalent of carboxyl group present in the aqueous emulsion polymer and derived from the total amount of monomers (a), (b), and (c) used in the production of the aqueous emulsion polymer.

50. A removable, water-whitening resistant pressure sensitive adhesive comprising a crosslinked aqueous emulsion polymer comprising:

- (a) about 70 to about 90 wt. % of at least one hydrophobic monomer selected from an alkyl (meth)acrylate ester of an alcohol wherein the alkyl portion of the alcohol is linear or branched and contains at least 4 carbon atoms, or a mixture of at least one styrenic monomer and at least one alkyl (meth)acrylate ester of an alcohol wherein the alkyl portion of the alcohol is linear or branched and contains at least 4 carbon atoms, wherein when a styrenic monomer is present, said styrenic monomer is present in an amount up to about 30 wt. % of the total hydrophobic monomer mixture;
- (b) about 2 to about 10 wt. % of at least one hydrophilic monomer; and
- (c) about 5 to about 25 wt. % of at least one partially hydrophilic

monomer selected from alkyl (meth)acrylate esters of an alcohol wherein the alkyl portion of the alcohol has 1 to 2 carbon atoms, N-vinyl-2-pyrrolidone, or mixtures thereof; and wherein said crosslinked aqueous emulsion polymer is crosslinked with at least one polyfunctional aziridine crosslinker, and the wt. % of monomers (a), (b), and (c) are based on the total weight of monomers (a), (b), and (c).

51. The composition of claim 50 wherein said aqueous emulsion polymer further comprises a surfactant selected from a non-polymerizable surfactant, a polymerizable surfactant, or mixtures thereof.

52. The composition of claim 51 wherein said surfactant comprises a non-polymerizable surfactant.

53. The composition of claim 52 wherein said non-polymerizable surfactant is selected from an ionic surfactant or a mixture of an ionic surfactant and a nonionic surfactant.

54. The composition of claim 53 wherein said ionic surfactant is an anionic surfactant selected from alkyl aryl sulfonates, alkyl sulfates, sulfates of ethoxylated alcohols, sulfates and sulfonates of ethoxylated alkylphenols, sulfosuccinates, diphenyl sulfonates, or mixtures thereof.

55. The composition of claim 51 wherein said surfactant is at least one water-soluble or water-dispersible polymerizable surfactant selected from compounds having a terminal allyl amine moiety, substituted phenyl compounds having at least one alkenyl substituent, polyoxyalkylene-1-(allyloxymethyl) alkyl ether sulfate salts, or mixtures thereof.

56. The composition of claim 51 wherein said surfactant is a mixture of an ionic non-polymerizable surfactant and a water-soluble or water-dispersible polymerizable surfactant selected from compounds having a terminal allyl amine moiety, substituted phenyl compounds having at least one alkenyl substituent, polyoxyalkylene-1-(allyloxymethyl) alkyl ether sulfate salts, or mixtures thereof.

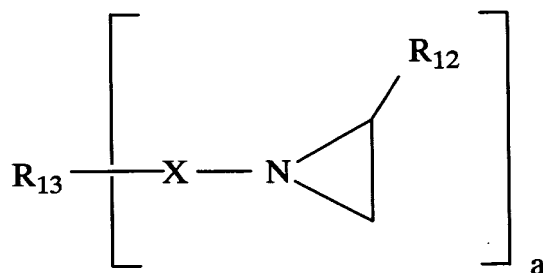
57. The composition of claim 50 wherein said polyfunctional aziridine is a compound having at least two nitrogen atoms wherein at least one of the nitrogen atoms is in an aziridine ring and at least one of the nitrogen atoms is contained in a side chain bonded to the aziridine nitrogen.

58. The composition of claim 57 wherein said polyfunctional aziridine is selected from N-aminoethyl-N-aziridylethylamine, N,N-bis-2-aminopropyl-N-aziridylethylamine, or N-3,6,9-triazanonyl-aziridine.

59. The composition of claim 50 wherein said polyfunctional aziridine is a compound having at least two aziridine groups.

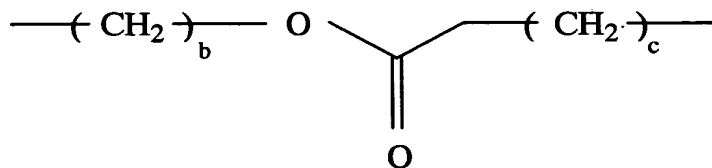
60. The composition of claim 59 wherein said polyfunctional aziridine is selected from bisaziridines of diacrylates of alkoxyated polyols, trisaziridines of triacrylates of alkoxyated polyols, or mixtures thereof.

61. The composition of claim 59 wherein said polyfunctional aziridine is selected from polyaziridines represented by the formula



wherein R_{12} is hydrogen or an alkyl group having 1 to 10 carbon atoms, optionally substituted by groups which do not interfere with the crosslinking reaction; R_{13} is a direct bond or an aliphatic radical having 1 to 30 carbon atoms, optionally substituted by hydroxy, halogen, or C_1 to C_{12} alkoxy; X is an alkylene group having 1 to 30 carbon atoms, optionally containing an ester group, an ether group, or an amide group; and a is 2 to 4.

62. The composition of claim 61 wherein R_{12} is selected from hydrogen, methyl, ethyl, propyl or butyl, X is represented by the formula



wherein b is 1 to 3 and c is 1 to 3; a is 2 to 3; and R_{13} is a propylene radical or a 2-hydroxyethyl radical.

63. The composition of claim 61 wherein said polyaziridine is selected from trimethylolpropane tris[([β]-N-aziridinyl)propionate], pentaerythritol tris[([β]-N-aziridinyl)propionate], trimethylolpropane tris[([β]-N-2-methyl-1-aziridinyl)propionate], or mixtures thereof.

64. The composition of claim 50 wherein the amount of aziridine groups in said polyfunctional aziridine crosslinker is at least 0.01 equivalents per equivalent of carboxyl group present in the aqueous emulsion polymer and derived from the total amount of monomers (a), (b), and (c) used in the production of the aqueous emulsion polymer.

65. A removable, water-whitening resistant pressure sensitive adhesive comprising a crosslinked aqueous emulsion polymer comprising:

- (a) about 70 to about 90 wt. % of at least one hydrophobic monomer selected from butyl acrylate, 2-ethylhexyl acrylate, mixtures of butyl acrylate and 2-ethylhexyl acrylate, or a mixture of styrene and at least one of butyl acrylate and 2-ethylhexyl acrylate, wherein when styrene is present, said styrene is present in an amount up to about 30 wt. % of the total hydrophobic monomer mixture;
- (b) about 2 to about 10 wt. % of at least one hydrophilic monomer selected from acrylic acid, methacrylic acid, 2-hydroxyethyl acrylate, or mixtures thereof;
- (c) about 8 to about 20 wt. % of at least one partially hydrophilic

- monomer selected from methyl acrylate, methyl methacrylate, or mixtures thereof; and
- (d) a surfactant selected from a non-polymerizable surfactant, a polymerizable surfactant, or mixtures thereof;
- 5 wherein said crosslinked aqueous emulsion polymer is crosslinked with at least one polyfunctional aziridine crosslinker, and the wt. % of monomers (a), (b), and (c) are based on the total weight of monomers (a), (b), and (c).
66. The composition of claim 65 wherein said surfactant is a non-
10 polymerizable surfactant.
67. The composition of claim 66 wherein said non-polymerizable surfactant is selected from an ionic surfactant or a mixture of an ionic surfactant and a nonionic surfactant.
68. The composition of claim 67 wherein said ionic surfactant is an
15 anionic surfactant selected from alkyl aryl sulfonates, alkyl sulfates, sulfates of ethoxylated alcohols, sulfates and sulfonates of ethoxylated alkylphenols, sulfosuccinates, diphenyl sulfonates, or mixtures thereof.
69. The composition of claim 65 wherein said surfactant is at least one water-soluble or water-dispersible polymerizable surfactant selected from compounds
20 having a terminal allyl amine moiety, substituted phenyl compounds having at least one alkenyl substituent, polyoxyalkylene-1-(allyloxymethyl) alkyl ether sulfate salts, or mixtures thereof.
70. The composition of claim 65 wherein said surfactant is a mixture of an ionic non-polymerizable surfactant and a water-soluble or water-dispersible
25 polymerizable surfactant selected from compounds having a terminal allyl amine moiety, substituted phenyl compounds having at least one alkenyl substituent, polyoxyalkylene-1-(allyloxymethyl) alkyl ether sulfate salts, or mixtures thereof.
71. The composition of claim 65 wherein said polyfunctional aziridine is a compound having at least two nitrogen atoms wherein at least one of the nitrogen

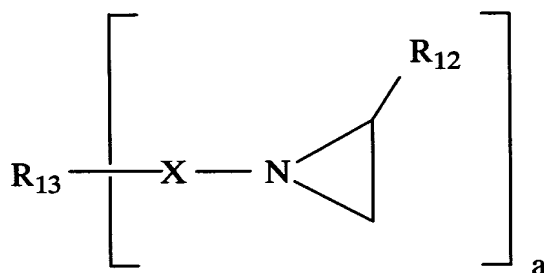
atoms is in an aziridine ring and at least one of the nitrogen atoms is contained in a side chain bonded to the aziridine nitrogen.

72. The composition of claim 71 wherein said polyfunctional aziridine is selected from N-aminoethyl-N-aziridilethylamine, N,N-bis-2-aminopropyl-N-aziridilethylamine, or N-3,6,9-triazanonyl-aziridine.

73. The composition of claim 65 wherein said polyfunctional aziridine is a compound having at least two aziridine groups.

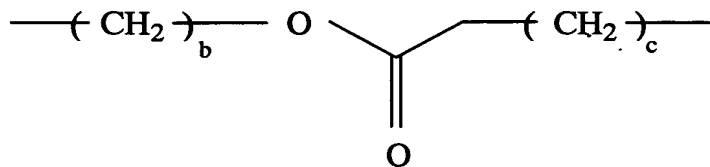
74. The composition of claim 73 wherein said polyfunctional aziridine is selected from bisaziridines of diacrylates of alkoxyated polyols, trisaziridines of triacrylates of alkoxyated polyols, or mixtures thereof.

75. The composition of claim 73 wherein said polyfunctional aziridine is selected form polyaziridines represented by the formula



wherein R₁₂ is hydrogen or an alkyl group having 1 to 10 carbon atoms, optionally substituted by groups which do not interfere with the crosslinking reaction; R₁₃ is a direct bond or an aliphatic radical having 1 to 30 carbon atoms, optionally substituted by hydroxy, halogen, or C₁ to C₁₂ alkoxy; X is an alkylene group having 1 to 30 carbon atoms, optionally containing an ester group, an ether group, or an amide group; and a is 2 to 4.

76. The composition of claim 75 wherein R₁₂ is selected from hydrogen, methyl, ethyl, propyl or butyl, X is represented by the formula



5 wherein b is 1 to 3 and c is 1 to 3; a is 2 to 3; and R₁₃ is a propylene radical or a 2-hydroxyethyl radical.

77. The composition of claim 75 wherein said polyaziridine is selected from trimethylolpropane tris[([β]-N-aziridiny)propionate], pentaerythritol tris[([β]-N-aziridiny)propionate], trimethylolpropane tris[([β]-N-2-methyl-1-aziridiny)propionate], or mixtures thereof.

10 78. The composition of claim 65 wherein the amount of aziridine groups in said polyfunctional aziridine crosslinker is at least 0.01 equivalents per equivalent of carboxyl group present in the aqueous emulsion polymer and derived from the total amount of monomers (a), (b), and (c) used in the production of the aqueous emulsion polymer.